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(12) **United States Patent**
Rexin et al.(10) **Patent No.:** **US 9,221,974 B2**
(45) **Date of Patent:** ***Dec. 29, 2015**(54) **REINFORCED POLYAMIDE MOULDING MATERIALS**(75) Inventors: **Ornulf Rexin**, Domat/Ems (CH);
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Manfred Hewel, Domat/Ems (CH)(73) Assignee: **EMS-CHEMIE AG**, Domat/EMS (CH)(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 618 days.

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See application file for complete search history.

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Primary Examiner — Bijan Ahvazi*Assistant Examiner* — David L Miller(74) *Attorney, Agent, or Firm* — Browdy and Neimark, PLLC(57) **ABSTRACT**

The present invention relates to reinforced polyamide molding materials which can be prepared from a polyamide blend and, for example, by compounding with cut fibers or continuous filaments on twin-screw extruders and have mechanical properties which are usually not compatible with one another, namely a combination of exceptionally high rigidity and strength and at the same time good toughness. Furthermore, a high heat distortion temperature (HDT) is achieved according to the invention.

The thermoplastic polyamide molding materials according to the invention are suitable for the production of moldings or other semifinished products or finished articles, which can be produced, for example, by extrusion, injection molding, direct methods or direct compounding, in which the compounded polyamide molding material is processed directly by injection molding, or other deformation techniques.

28 Claims, No Drawings

REINFORCED POLYAMIDE MOULDING MATERIALS

The present invention relates to reinforced polyamide moulding materials which can be prepared from a polyamide blend and, for example, by compounding with cut fibres or continuous filaments on twin-screw extruders and have mechanical properties which are usually not compatible with one another, namely a combination of exceptionally high rigidity and strength and at the same time good toughness. Furthermore, a high heat distortion temperature (HDT) is achieved according to the invention.

The thermoplastic polyamide moulding materials according to the invention are suitable for the production of mouldings and other semifinished products or finished articles, which can be produced, for example, by extrusion, injection moulding, pressing, direct processes or direct compounding, in which the compounded polyamide moulding material is processed directly by injection moulding, or other deformation techniques.

Reinforced polyamide blends are playing an increasing role in the area of technical construction materials since they exhibit good toughness and heat distortion temperature in addition to high rigidity. Fields of use are, for example, interior and exterior parts in the automotive sector and in the area of other means of transport, housing materials for devices and apparatuses for telecommunications, entertainment electronics, household appliances, mechanical engineering, heating sector and fixing parts for installations.

The particular advantage of reinforced polyamides lies in the exceptionally good bond between polymer matrix and reinforcing materials. This also applies in the case of high degrees of reinforcement which lead to high rigid products. However, the toughness of these products does not meet all requirements.

Below, polyamides are to be understood as meaning those polymers which are derived from dicarboxylic acids, diamines, aminocarboxylic acids and/or lactams. They may be homo- or copolyamides. The number average molecular weight of the polyamides should be above 5000, preferably above 10 000.

JP 07-097514 (Asahi) describes polyamide resin compositions as insulation material for electrical sliding switches. The property profile strived for includes the following properties: dimensional stability, HDT, creep resistance, arc resistance, surface roughness, surface gloss, deposits in the mould during shaping, frictional properties and flowability. Particular value is attached to the electrical properties, the surface quality and the frictional properties. The polyamide blend used as a matrix (40 to 70% by weight) is composed of (a1) a copolyamide of 55 to 95% by weight of 66 units and 5 to 45% by weight of 6I units and/or 6 units and (a2) 0 to 50% by weight of an aliphatic polyamide (PA) selected from PA6, PA66, PA11, PA12, PA610, PA612, PA46 and, as a filler (30 to 60% by weight), a mixture of fibres and minerals (weight ratio 1.0 or lower) selected from glass fibres, carbon fibres, mica, talc, kaolin, wollastonite, calcium carbonate, magnesium oxide or potassium titanate. In the examples, copolyamide 66/6I or copolyamide 66/6 is used as component (a1) and PA66, PA66/6, PA612 or PA6 is used as component (a2). The ultimate tensile strengths achieved in the examples are between 1070 kg/cm² and 1800 kg/cm², i.e. between 105 MPa and 176 MPa. The HDT A values achieved are between 210° C. and 241° C.

JP 03-269056 (Mitsubishi) describes very generally in the patent claims polyamide moulding materials comprising (A) polyamide 6 or polyamide 66 in combination with a copolya-

mid of (Ba) aliphatic diamine, isophthalic acid and terephthalic acid (60 to 100% of (Ba)) and (Bb) lactam and/or aliphatic diamine and aliphatic dicarboxylic acid (0 to 40% of (Bb)), filler (C) and, as component (D), saturated aliphatic carboxylic acids and/or a metal salt thereof. According to JP 03-269056, the conditions (A)+(B)=40 to 95%, (C)=3 to 60%, (D)=0.005 to 1% and a ratio of (B)/(A) of 0.01 to 0.025, where (B)=(Ba)+(Bb), are applicable for the ratios. However, according to the practical formulations worked in the examples of JP 03-269056, either polyamide 66 or polyamide 6 is used as the aliphatic polyamide, while a polyamide 6I/6T (weight ratio 66.7/33.3) or a polyamide 6I/6T/6 (weight ratio 62.6/31.3/6.1) is used as the semi-aromatic polyamide. Exclusively glass fibres, optionally in combination with wollastonite, are used as the filler, the maximum content of filler being 40% by weight (cf. examples 2 and 3). According to JP 03-269056, it is intended to provide moulding materials which have outstanding thermal and mechanical behaviour and also exhibit good surface properties, i.e. do not show any deformation or sink marks in the mouldings. According to JP 03-269056 (cf. example 2), however, only a HDT/A of 241° C. and an HDT/C of 150° C. are achieved with the use of 6I/6T (for re-working by the inventor, see comparative example 11). Moreover, ultimate tensile strengths of 182 and 185 MPa, respectively (cf. examples 2 and 3) are obtained.

It is therefore an object of the present invention to provide high rigid and at the same time tough, reinforced polyamide moulding materials having high heat distortion temperatures (HDT) so that a certain filler content results in mechanical properties which are usually not compatible with one another.

This object is achieved by the fibre-reinforced polyamide blend according to claim 1, comprising a polyamide matrix of a blend of polyamide 66 (homopolyamide) and a copolyamide (CoPA) 6T/6I (B) and, as reinforcing material, a mixture of glass fibres and carbon fibres. According to the invention, in order to obtain a further increase in the rigidity, a part of the glass fibres was replaced by carbon fibres so that a hybrid fibre-reinforced compound is used.

The object is furthermore achieved by the method for manufacturing moulding materials according to claim 12, 13 or 14 by the long fibre-reinforced rod-shaped pellets according to claim 15, the application is archived according to claim 16, the manufacturing of the moulding materials according to claim 17 as well as the moulding materials according to claim 18.

The subclaims contain advantageous but not exclusive embodiments of the invention.

The polyamide moulding materials according to the invention are therefore high rigid and at the same time tough, reinforced polyamide moulding materials having high heat distortion temperature (HDT), containing, as polyamide matrix, a blend of the following components:

(A) polyamide 66,

(B) copolyamide, composed of

(b₁) 50 to 80 parts by weight of units, in particular 50 to 70 parts by weight of units, which are derived from terephthalic acid (T) in combination with hexamethylenediamine (6) in almost equimolar ratio,

(b₂) 50 to 20 parts by weight of units, in particular 50 to 30 parts by weight of units, which are derived from isophthalic acid (I) in combination with hexamethylenediamine in almost equimolar ratio,

the parts by weight of the components (b₁) and (b₂) together giving 100 parts by weight,

and containing, as filler component, a mixture of:

(C) glass fibres and

(D) carbon fibres,

the percentages by weight of the components (A) to (D) together giving 100% and the components (A), (B), (C), and (D) fulfilling the following conditions:

(A)+(B): 20 to 60% by weight, in particular 20 to 39% by weight,

weight ratio (A)/(B): 50/50 to 95/5,

(C)+(D): 40 to 80% by weight,

weight ratio (C)/(D): 80/20 to 95/5,

the polyamide moulding materials optionally containing additives (E) in addition to the components (A) to (D), and the amount thereof being additive to the sum of the components (A) to (D).

In special embodiments of the invention the amount of filler i.e. of glass fibres and carbon fibres is 61 to 75% by wt, particularly preferred 64 to 75% by wt., exceptionally preferred 66 to 75% by wt.

The mechanical and thermal properties of the reinforced moulding materials obtained according to the invention comprise ultimate tensile strengths of above 230 MPa (measured at norm test specimens according to ISO 527), elongation at break of above 1.4% (measured at norm test specimens according to ISO 527), thermal deformation resistance values HDT/A (1.8 MPa) (measured according to ISO 75) of above 242° C., preferred of at least 245° C., HDT/C (8 MPa) (measured according to ISO 75) of above 165° C., preferred of above 190° C.

As copolyamide a copolyamide 6T/6I (component (B)) is used according to the invention. The ratio of polyamide 6T/6I to the proportion polyamide 66 is of particular importance.

The melting point and the HDT can be raised by adjustment of the ratio 6T>6I. The copolyamide shows a relative viscosity (RV) measured in 0.5% m-cresol solution of between 1.4 and 1.8, preferably of 1.48 to 1.7.

The glass fibres used as filling components (C) according to the invention show an diameter of 5 to 20 µm, preferably of 5 to 10 µm, in which the cross section of the glass fibres is round, oval or angled. Especially, according to the invention, E glass fibres are used. However, all other kinds of glass fibres, such as A, C, D, M, S, R glass fibres or any compositions thereof or compositions with E glass fibres can be applied.

However, the moulding materials according to the invention can also comprise additives (E), such as from the group consisting of inorganic stabilizers, organic stabilizers, lubricants, dyes, metallic pigments, metal spangles, metal-coated particles, halogen-containing flameproofing agents, halogen-free flameproofing agents, impact modifiers, antistatic agents, conductivity additives, demoulding agents, optical brighteners, natural sheet silicates, synthetic sheet silicates or mixtures of said additive.

Antistatic agents which may be used in the moulding materials according to the invention are, for example, carbon black and/or carbon nanotubes.

The use of carbon black in addition to the carbon fibres present can, however, also serve for improving the blackness of the moulding material.

Sheet silicates which may be used in the moulding materials according to the invention are, for example, kaolins, serpentines, talc, mica, vermiculites, illites, smectites, montmorillonite, hectorite, double hydroxides or mixtures thereof. The sheet silicates may have been surface-treated or may be untreated.

Stabilizers or antiaging agents which may be used in the moulding materials according to the invention are, for example, antioxidants, antiozonants, light stabilizers, UV stabilizers, UV absorbers or UV blockers.

The present invention therefore relates to a fibre-reinforced polyamide blend having mechanical properties which are usually not compatible with one another, namely a combination of exceptionally high rigidity and high HDT and at the same time good toughness.

Surprisingly, it has been found that this can be achieved by the combination of two measures: the addition of a partly aromatic copolyamide 6T/6I and the use of carbon fibres in addition to glass fibres. Thus, a hybrid fibre-reinforced compound is used, a content of 15 to 30% by weight of PA66, 4 to 17% by weight of CoPA 6T/6I, 61 to 65% by weight of glass fibres and 5 to 9% by weight of carbon fibres having been found to be a particularly preferred composition for the moulding material according to the invention, with regard to both mechanical properties and cost-efficiency. The percentages by weight sum to 100%. The amount of any additives is in addition to this 100%.

In an embodiment of the invention with a total fibre content of 66 to 74% by weight, the moulding materials exhibit a tensile modulus of elasticity of more than 25 500 MPa, preferably of more than 27 000 MPa, particularly preferably of more than 28 000 MPa, and in particular an elongation at break of at least 1.5%.

The elongation at break of the moulding materials according to the invention having a total fibre content of 66 to 74% by weight may be preferably at least 1.7%, particularly preferably at least 1.8%.

In particular, the impact strength (Charpy New, 23° C.) of the moulding materials according to the invention having a total fibre content of 66 to 74% by weight is at least 50 kJ/m², preferably at least 60 kJ/m², particularly preferably at least 70 kJ/m².

In another embodiment of the invention, the moulding materials according to the invention having a filler content (total fibre content) of 46 to 54% by weight have a tensile modulus of elasticity of more than 18 000 MPa, preferably of more than 19 000 MPa, particularly preferably of more than 20 000 MPa, and in particular an elongation at break of at least 2.0%.

Particularly preferably, the elongation at break of the moulding materials according to the invention having a total fibre content of 46 to 54% by weight is at least 2.3%, very particularly preferably at least 2.5%.

The impact strength (Charpy New, 23° C.) of the moulding materials according to the invention having a total fibre content of 46 to 54% by weight is in particular at least 65 kJ/m², preferably at least 80 kJ/m², particularly preferably at least 90 kJ/m².

The values of the tensile modulus of elasticity are greatly dependent on the total fibre content, the glass fibre/carbon fibre mixing ratio and the mixing ratio of the two polyamides PA66 and PA6T/6I.

Particularly highly reinforced compounds are usually very brittle and not suitable for practical use. Surprisingly, it has been found that there are possible blend combinations which impart exceptionally good toughness, i.e. elongation at break or impact strength, to the compound in spite of high fibre content, very high rigidity and high HDT.

It has been found according to the invention that in particular a mixture of an aliphatic PA 66 having a relative viscosity between 2.3 and 2.7 measured in H₂SO₄, 1%) and a partly aromatic CoPA 6T/6I in the ratio 70:30 has a particularly preferred combination of extremely high rigidity, good toughness and high HDT. Finally, according to the invention, a product having even more metal-like properties than glass fibre-reinforced materials to date is disclosed.

An even higher toughness and hence an even more metal-like property can be achieved with the use of especially thin glass fibres having a diameter of less than 10 μm .

In long fibre-reinforced moulding materials higher toughnesses result and thus even more metal-like properties, if instead of the common endless glass fibre with a diameter of 15 to 19 μm such with a diameter of 10 to 14 μm , preferably such with a diameter of 10 to 12 μm are used.

The preparation of the polyamide moulding materials according to the invention can be effected on customary compounding machines, such as, for example, single-screw or twin-screw extruders or screw kneaders. As a rule, the polymeric fraction is first melted and the reinforcing material (glass fibres and carbon fibres) can be introduced at the same point or at different points of the extruder, for example by means of a side feeder. The compounding is preferably effected at set barrel temperatures of 280° C. to 320° C. The polymeric fraction and the reinforcing material can, however, also be metered together into the feed.

The polyamide moulding materials according to the invention can furthermore be prepared by the known methods for manufacturing long fibre-reinforced rod-shaped pellets particularly manufactured by pulltrusion method, wherein the endless fibre strand (roving) is completely saturated with the polymer melt and afterwards cooled down and cut. The long fibre-reinforced rod-shaped pellets obtained in this way, which preferably shows a granulate length of 4 to 25 mm, especially of 5 to 12 mm, can be processed by the common processing methods (such as injection moulding, pressing) to shaped articles, in which especially fine properties of the shaped article are obtained by mild processing methods. In this context mild means mainly that an excessive fibre fracture and the strong reduction of the fibre length associated with it is largely avoided. For the injection moulding this means that screws with large diameter and low compression ratio, especially below 2, and nozzle and Angus ducts dimensioned on a grand scale are preferably used. Additional it has to made sure that the rod-shaped pellets flux on quickly (contact heating) via high cylinder temperatures and the fibres are not to much hackled due to excessive shear stress. Bearing in mind these measures, shaped articles are obtained according to the invention, which show in average a larger fibre length than comparable shaped articles made from short fibre-reinforced moulding materials. Through this, an additional improvement of the properties, especially tensile modulus of elasticity, the ultimate tensile strength and the notch impact toughness is obtained.

The polymer extrudate produced from moulding materials according to the invention can be processed by all known pelletizing methods to give pellets, such as, for example, by pelletizing in which the extrudate is cooled in a water bath and then cut. From a fibre content of more than 60% by weight, the use of underwater pelletizing or hot face cutting under water, in which the polymer melt is forced directly through a die and pelletized by a rotating knife in a water stream, is advisable for improving the pellet quality.

A further possibility for the preparation of the moulding materials according to the invention is the mixing of pellets with, for example, different matrices and/or fillers to give a dry blend which is subsequently further processed. For example, in each case a compound in pellet form can first be prepared from the components (A) and/or (B) and the fillers (C) and/or (D) and optionally the additive (E), and these pellets can then be mixed to give a dry blend, optionally with addition of even further amounts of component (A) and/or (B) in pellet form. The dry blend prepared in this manner is then further processed (cf. Claim 13).

The homogenized pellet mixture (dry blend) is processed in a processing machine, for example a screw injection moulding machine, to give hybrid fibre-reinforced mouldings and/or hollow bodies, it being possible to add further amounts of component (A) and/or (B) in pellet form.

With the processing of a dry blend, better mechanical properties tend to be achieved. However, the mixing of the dry blend gives rise to an additional production step which increases the production costs and hence adversely affects the cost-efficiency. Moreover, vibrations during transport may result in separation, caused by the difference between the densities of the various types of pellets.

The mouldings produced from the moulding materials according to the invention are used for the production of interior and exterior parts, preferably having a supporting or mechanical function, in the electrical, furniture, sport, mechanical engineering, sanitary and hygiene areas, medicine, energy and drive technology, in the automotive sector and the sector relating to other means of transport, or housing material for devices and apparatuses for telecommunication, entertainment electronics, household appliances, mechanical engineering, the heating sector or fixing parts for installations or for containers and ventilation parts of all types.

In particular the area of metal die casting replacement in which extremely high rigidity in combination with good toughness is expected may be mentioned as possible applications for the mouldings produced from the moulding materials according to the invention.

Processing Methods

In addition to the customary processing methods, such as extrusion or injection moulding, the following processing methods are also suitable:

Coinjection/bi-injection or assembly injection moulding for hybrid parts in which the polyamide moulding material according to the invention is combined with other compatible or incompatible materials, such as, for example, thermoplastics, thermosetting plastics or elastomers.

Insert parts, such as, for example, bearing parts or thread inserts comprising the polyamide moulding material according to the invention, coated with other compatible or incompatible materials, such as, for example, thermoplastics, thermosetting plastics or elastomers.

Outsert parts, such as frames, housings or supports comprising the polyamide moulding material according to the invention into which functional elements comprising other compatible or incompatible materials, such as, for example, thermoplastics, thermosetting plastics or elastomers, are injected.

Hybrid parts (elements comprising the polyamide moulding material according to the invention in combination with other compatible or incompatible materials, such as, for example, thermoplastics, thermosetting plastics or elastomers), produced by sandwich injection moulding, injection welding, assembly injection moulding, ultrasonic, friction or laser welding, adhesive bonding, flanging or riveting.

Semifinished products and profiles (for example produced by extrusion, pultrusion, arrangement in layers or lamination).

Surface coating, lamination, chemical or physical metallization, flocking, it being possible for the polyamide moulding material according to the invention to be the substrate itself or the substrate support or, in the case of hybrid/bi-injection parts, a defined substrate region, which can also be brought to the surface by subsequent

chemical (e.g. etching) or physical treatment (for example cutting or laser ablation).

Printing, transfer printing, 3-D printing, laser inscription.

Applications

Electrical Appliance Sector

Stop and/or adjusting elements for electrical hand tools with or without integrated electrical functions (moulded interconnect devices, MID)

connecting rods and/or pistons for hammer drills in homogenous design, i.e. comprising one material, or as a hybrid part, i.e. comprising a combination of materials housings, gear housings for right angle grinders, drills, electric planes or grinding machines with or without integrated electrical functions (MID) in homogeneous design or as a hybrid part, it being possible for certain functional areas (e.g. force transmission surfaces, sliding surfaces, decorative layer areas, grip region) to comprise another compatible or incompatible material (e.g. for targeted delamination or deformation, predetermined breaking point, force or torque limitation)

tool holders, e.g. chucks or fixing means

sewing machine housings, sliding tables with or without integrated electrical functions (MID)

Sanitary and Hygiene Sector

Housings and/or functional elements (e.g. for pumps, gears, valves) for oral irrigators, toothbrushes, comfort toilets, shower cabinets, hygiene centres with or without integrated electrical functions (MID) in homogeneous design or as a hybrid part

Household Appliance Sector

Housings and/or functional elements for mechanical, electrical or electromechanical closing systems, locking systems or sensors with or without integrated electrical functions (MID) for

refrigerators, chest refrigerators, chest freezers

ovens, cookers, steam cookers

dishwashing machines

Automotive Sector

Housings and/or holders with or without integrated electrical functions (MID) in homogenous design or as a hybrid part for

controls/switches (e.g. for exterior mirror adjustment, seat position adjustment, lighting, driving direction indicator)

interior sensors, e.g. for seat occupation

exterior sensors (e.g. for parking aids, ultrasonic or radar distance meters)

sensors in the engine space (e.g. vibration or knocking sensors)

interior and exterior lights

motors and/or drive elements in the interior and exterior area (e.g. for seat comfort functions, exterior mirror adjustment, headlight adjustment and/or tracking, curve light)

monitoring and/or control systems for vehicle drive (e.g. for media transport and/or regulation of, for example, fuel, air, coolant, lubricant)

mechanical functional elements and/or sensor housings with or without integrated electrical functions (MID) for closing systems, locks, pull-to systems, e.g. in the case of vehicle swivel doors, sliding doors, engine space flaps or hoods, tailgates, vehicle windows

Mechanical Engineering

ISO standard parts and/or machine elements (e.g. screws, nuts, bolts, wedges, shafts, gear wheels) in standard dimensions or application-specific design or homogenous design

ISO standard parts and/or machine elements, such as, for example, screws, nuts, bolts, wedges, shafts in standard dimensions or application-specific design or as a hybrid part, it being possible for certain functional regions, such as, for example, force transmission surfaces, sliding surfaces, decorative layer areas, to comprise another compatible or incompatible material (for example for targeted delamination, predetermined breaking point, force/torque limitation)

supports, stands, plinths for processing machines, such as, for example, upright drilling machines, table drilling machines, cutting machines or combination machines for metal and/or wood processing

insert parts, e.g. threaded bushes

self-tapping screws

Energy and Drive Technology Sector:

frames, housings, support parts (substrate) and/or fixing elements for solar cells with or without integrated electrical functions (MID) in homogeneous design or as a hybrid part

tracking and/or adjusting elements (e.g. for bearings, hinges, joints, drawbars, bumpers) for collectors.

pump housings and/or valve housings with or without integrated electrical functions (MID) in homogenous design or as a hybrid part.

Medical Equipment Sector

frames, housings, support parts with or without integrated electrical functions (MID) in homogeneous design or as a hybrid part for monitoring devices and/or equipment for supporting vital functions

disposable instruments, such as, for example, scissors, clamps, forceps, knife handles in homogeneous design or as a hybrid part

constructions for short-term or emergency fixing of fractures in homogeneous design or as a hybrid part

walking aids with or without integrated electrical functions (MID) and/or sensors for load monitoring in homogeneous design or as a hybrid part.

Sanitary Sector

pump housings, valve housings or water meter housings with or without integrated electrical functions (MID) in homogeneous design or as a hybrid part.

The following examples are intended to explain the invention but without limiting it.

EXAMPLES

The materials used in the examples and comparative examples are characterized in table 1.

TABLE 1

Material	Trade Name	Relative viscosity 20° C. m-cresol, 0.5%	Composition % by weight	Manufacturer
PA66	Radipol A45	2.7 in H ₂ SO ₄ , 1%	—	Radici Chimica, Italy
PA6T/6I	XE 3733 NK	1.56	70/30	EMS-CHEMIE AG, Switzerland
GF	Vetrotex EC10-4.5MM 99B	—	—	Saint-Gobain Vetrotex, France
CF	Tenax HTA 5N51 6MM	—	—	Toho Tenax Europe GmbH, Germany

TABLE 1-continued

Material	Trade Name	Relative viscosity 20° C. m-cresol, 0.5%	Composition % by weight	Manufacturer
PA6I/6T	GRIVORY G21	1.52	2/1	EMS-CHEMIE AG, Switzerland
PA6	GRILON A23	2.47 in H ₂ SO ₄ , 1%	—	EMS-CHEMIE AG, Switzerland

GF Glass fibre
CF Carbon fibre

The moulding materials having the compositions in Table 2 are prepared on a ZSK 25 type twin-screw extruder from Werner and Pfleiderer. The PA66 and PA6T/6I pellets are metered into the feed zone. The glass fibre, like the carbon fibre, is metered into the polymer melt via a side feeder 3 barrel units before the die.

The barrel temperature was set as an ascending profile up to 310° C. At 150 to 200 rpm, a 10 kg throughput was used. After the extrudates had been cooled in a water bath and following pelletizing and drying at 120° C. for 24 h, the pellet properties were measured.

The test specimens were produced on an Arburg injection moulding unit, the cylinder temperatures of 310° C. to 320° C. and a circumferential screw velocity of 15 m/min being set. The mould temperature was chosen as 110° C.

The mechanical properties, tensile modulus of elasticity, ultimate tensile strength and elongation at break, were determined by a tensile test on standard test specimens according to ISO 527. The measurement of the impact strength (IS) was carried out according to Charpy at 23° C. based on ISO 179/2-1eU.

The determination of the HDT/A (1.8 MPa) and HDT/C (8 MPa) was carried out according to ISO 75.

TABLE 2

Property	Examples No.									
	1	2	3	4	5	6	7	8	9	10
PA66 % by wt.	25	33	25	33	18	22.7	18	24	16	20
PA6T/6I % by wt.	25	17	25	17	14	7.3	12	6	14	10
Glass fibre % by wt.	42	42	43.5	43.5	58	62	62	64	64	64
Carbon fibre % by wt.	8	8	6.5	6.5	10	8	8	6	6	6
Tensile modulus of elasticity MPa	20500	20000	19100	19400	28800	28600	28800	28300	28200	28300
Ultimate tensile strength MPa	250	250	250	250	240	260	250	245	245	245
Elongation at break %	2.5	2.5	2.5	2.5	1.8	1.8	1.8	1.7	1.8	1.7
Charpy New impact 23° C. kJ/m ²	80	90	90	95	65	70	70	60	60	65
HDT A ° C.	245	255	245	245	245	245	245	245	245	245
HDT C ° C.	185	190	185	200	215	215	215	195	200	195

TABLE 3

Property	Comparative Examples No.					
	11	12	13	14	15	16
PA66 % by wt.	50	37		28		23
PA6T/6I % by wt.			50			
PA6I/6T % by wt.	10	12		10		7
PA6 % by wt.					35	
Glass fibre % by wt.	40	50	50	60	65	70
Tensile modulus of elasticity MPa	14000	17000	17600	20000	22600	25000
Ultimate tensile strength MPa	215	250	250	250	210	240
Elongation at break %	2.8	2.5	2.0	2.2	1.6	1.5
Charpy New impact 23° C. kJ/m ²	65	90	80	70	45	60
Charpy New notch impact 23° C. kJ/m ²	11	12	10	14	12	10
HDT A ° C.	240	235	285	235	210	240
HDT C ° C.	150	165	210	175	180	190

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Examples 1 to 10 according to the invention show a more balanced property profile compared with comparative examples 11 to 16 with a corresponding filler content (i.e. a more balanced combination of high tensile modulus of elasticity and high HDT with simultaneously good elongation at break.

The moulding material of comparative example 13 comprising 50% by weight of filler shows a very high HDT value but has a substantially lower tensile modulus of elasticity and a substantially lower elongation at break than the moulding materials of examples 1 to 4 according to the invention.

The moulding material of comparative example 16 comprising 70% by weight of filler is below the moulding materials of examples 6 to 10 according to the invention in all measured values.

Particularly good mechanical properties are obtained on using especially thin glass fibres having a diameter of less than 10 μm . In this way, it is possible to increase in particular the toughness of the material by up to 15%.

TABLE 4

Property	Examples No.				
	17	18	19	20	21
PA66 % by wt.	37.5	30	26.25	22.5	26.25
PA6T/6I % by wt.	12.5	10	8.75	7.5	8.75
Glass fibre % by wt.	43	52	56	60	56
Carbon fibre % by wt.	7	8	9	10	9
Tensile modulus of elasticity MPa	20400	25200	30700	33400	29500
Ultimate tensile strength MPa	310	320	290	260	320
Elongation at break %	1.9	1.7	1.8	1.5	1.6
Charpy New impact 23° C. kJ/m ²	85	90	85	90	120
Charpy New notch impact 23° C. kJ/m ³	30	45	50	45	60

The examples quoted in table 4 are manufactured by the pultrusion method. The pultrusion conditions are listed in the following table:

temperature setting extruder and impregnating chamber	° C.	280-370
turnover pellets	kg/h	100-180
take-off velocity	m/min	5-11
fibre preheating	° C.	none
pellet length	mm	11

The test specimens manufactured from the long fibre-reinforced rod-granulate (granulate length 11 mm) show with appropriate fibre content still more improvements concerning the tensile modulus of elasticity, the ultimate tensile strength, the notch impact toughness compared to the comparative variants. For the impact toughness equal or higher values are obtained.

The measurement of the notch impact toughness has been performed according to Charpy at 23° C. as per ISO 179/2-1eA.

The glass fibres used in the pultrusion method as roving, show a diameter of 10 to 20 μm , preferred 12 to 18 μm , in which the cross section of the glass fibres is round, oval or angled. Especially, according to the invention, E glass fibres are used. However, all other kinds of glass fibres, such as A, C,

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D, M, S, R glass fibres or any compositions thereof or compositions with E glass fibres can be applied. The endless carbon fibres used in the pultrusion method show a diameter of 5 to 10 μm , preferably 6 to 8 μm .

To speed up the fibre impregnation, the fibres can be preheated to temperatures up to 400° C. via a convenient IR-, contact-, radiation- or hot gas-preheating. Apparatuses with spreading surfaces inside the impregnating chamber provide a complete impregnation of the fibres with the polymer melt. Strands, leaving the impregnating device can be formed by controlled cylinder systems, so that pellets with round, elliptic or rectangular cross section are obtained.

To improve the matrix connection and the fibre handling, the fibres can be coated with chemical different layers, as they are known for glass and carbon fibres in the state of the art.

For the examples 17 to 20 the glass fibre PPG 4588 with 17 μm diameter from the firm PPG Industries Fibre Glass has been used.

For the example 21 the glass fibre Vetrotex Roving RO99 with 12 μm diameter from the firm Saint Gobain Vetrotex has been used.

As carbon fibre in the examples 17 to 21 Tenax HTA 5131 with 7 μm diameter from the firm Toho Tenax Europe GmbH in form of a roving has been used.

The invention claimed is:

1. High rigid and simultaneously tough, reinforced polyamide moulding material, characterized by:

heat distortion temperature values HDT/A (1.8 MPa) (measured according to ISO 75) of more than 242° C., and HDT/C (8 MPa) of more than 150° C., consisting of (1) a polyamide matrix consisting of a blend of the following components:

(A) polyamide 66,
(B) copolyamide, composed of
(b₁) 50 to 80 parts by weight of units which are derived from terephthalic acid (T) in combination with hexamethylenediamine (6) in approximately equimolar ratio,
(b₂) 50 to 20 parts by weight of units which are derived from isophthalic acid (I) in combination with hexamethylenediamine in approximately equimolar ratio,
wherein the copolyamide has a relative viscosity (RV), measured in 0.5% m-cresol solution, of between 1.4 and 1.8;

the parts by weight of the components (b₁) and (b₂) together giving 100 parts by weight,
and (2) a filler component containing a mixture of:

(C) glass fibres and
(D) carbon fibres,
the percentages by weight of the components (A) to (D) together giving 100% and the components (A), (B), (C), and (D) fulfilling the following conditions:

(A)+(B): 20 to 39% by weight,
weight ratio (A)/(B): 50/50 to 95/5,
(C)+(D): 61 to 80% by weight,
weight ratio (C)/(D): 80/20 to 95/5,
the polyamide moulding material optionally containing (3) at least one additive (E) in addition to the components (A) to (D), and the amount thereof being additive to the sum of the components (A) to (D);

wherein the optional additive (E) is selected from the group consisting of inorganic stabilizers, organic stabilizers, lubricants, dyes, metallic pigments, metal spangles, metal-coated particles, halogen-containing flameproofing agents, halogen-free flameproofing agents, impact modifiers, antistatic agents, conductivity additives, demoulding agents, optical brighteners, natural sheet silicates, synthetic sheet silicates and mixtures thereof.

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2. Polyamide moulding material according to claim 1, characterized by ultimate tensile strength of more than 230 MPa (measured on standard test specimens according to ISO 527) and optionally elongation at break of more than 1.4% (measured on standard test specimens according to ISO 527).

3. Polyamide moulding material according to claim 1, characterized by a total fibre content of 66 to 74% by weight, a tensile modulus of elasticity of more than 25 500 MPa, and optionally an elongation at break of at least 1.5%.

4. Polyamide moulding material according to claim 1, characterized by a total fibre content of 66 to 74% by weight and an elongation at break of at least 1.7%.

5. Polyamide moulding material according to claim 1, characterized by a tensile modulus of elasticity of more than 18 000 MPa, and optionally an elongation at break of at least 2.0%.

6. Polyamide moulding material according to claim 1, characterized by an elongation at break of at least 2.3%.

7. Polyamide moulding material according to claim 1, in which the copolyamide is copolyamide 6T/6I and has a relative viscosity (RV), measured in 0.5% m-cresol solution, of between 1.48 and 1.7.

8. Polyamide moulding material according to claim 1, in which the glass fibres have a diameter of 5 to 20 μm .

9. Polyamide moulding material according to claim 1, characterized in that said antistatic agents are present and comprise carbon black and/or carbon nanotubes in amounts of up to 10% by weight.

10. Process for the preparation of the polyamide moulding material according to claim 1, comprising compounding the molding material at a set extruder barrel temperature 280° C. to 320° C., the polymeric components first being melted and cut fibres or continuous filaments then being introduced.

11. Process for the preparation of the polyamide moulding material according to claim 1, characterized in that for the fabrication of long fibre-reinforced rod-granulate by pultrusion, an endless fibre strand is completely impregnated with the polymer melt, subsequently cooled down and cut, so that long fibre-reinforced rod-granulate is obtained.

12. Process for the preparation of the polyamide moulding material according to claim 1, characterized in that initially a compound in granulate form is made from the components (A) and/or (B) and the fillers (C) and/or (D) and optionally the additive (E), and these granulates are subsequently admixed, in which still other amounts of granulate of component (A) and/or (B) are added optionally, and the granulate is further processed.

13. Long fibre-reinforced rod-shaped pellets obtained by pultrusion method according to claim 11, which has a granulate length of 4 to 25 mm.

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14. A method comprising molding the moulding material of claim 1 having an ultimate tensile strength of above 230 MPa (measured at norm test specimens according to ISO 527), elongation at break of above 1.5% (measured at norm test specimens according to ISO 527), thermal deformation resistance value HDT/A (1.8 MPa) (measured according to ISO 75) of above 242° C., HDT/C (8 MPa) (measured according to ISO 75) of above 165° C., for the fabrication of shaped articles and/or hollow parts.

15. Production of shaped articles and/or hollow parts from the polyamide moulding material according to claim 1, by extrusion, injection moulding, pressing or direct compounding.

16. A shaped article, obtained from the polyamide moulding materials according to claim 1.

17. The reinforced polyamide moulding material of claim 1 having the heat distortion temperature values HDTA (1.8 MPa) of at least 245° C. and HDT/C (8 MPa) more than 170° C. wherein

in said (B) there are 50-70 parts by weight, relative to the weight of (B), of units (b_1) which are derived from terephthalic acid (T) and 50-30 parts by weight, relative to the weight of (B), of units (b_2) which are derived from isophthalic acid (I).

18. The polyamide moulding material of claim 1 wherein (C)+(D) is 61-75% by weight.

19. The polyamide moulding material of claim 1 wherein (C)+(D) is 64-75% by weight.

20. The polyamide moulding material of claim 1 wherein (C)+(D) is 66-75% by weight.

21. The polyamide moulding material according to claim 3 wherein the tensile modulus of elasticity is more than 28,000 MPa.

22. The polyamide moulding material of claim 4 wherein the elongation at break is at least 1.8%.

23. The polyamide moulding material according to claim 4 wherein the tensile modulus of elasticity is more than 20,000 MPa.

24. The polyamide moulding material of claim 6 wherein the elongation at break is at least 2.5%.

25. The polyamide moulding material of claim 9 wherein the glass fibres have a diameter of 5-10 μm .

26. Polyamide moulding material according to claim 8, wherein the glass fibers are E-glass fibres.

27. Long fibre-reinforced rod-shaped pellets according to claim 13, which has a granulate length of 5 to 12 mm.

28. Polyamide moulding material according to claim 8, in which the glass fibres have a cross-section being round, oval or rectangular.

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